

5.3/00

5(4)  
AUTHORS:

67923  
SOV/20-129-5-33/64  
Voyevodskiy, V. V., Corresponding Member, AS USSR,  
Solodovnikov, S. P., Chibrikov, V. M.

TITLE:

Investigation of the Spectra of the Electron Paramagnetic Resonance (e.p.r) of the Negative Ions of Some Aromatic and Heterocyclic Compounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5, pp 1082-1084 (USSR)

ABSTRACT:

The purpose of this paper was to investigate the electron mobility along the systems of conjugate double bonds and saturated bonds by means of the e.p.r.-spectra. The authors investigated the e.p.r.-spectra of some benzene derivatives. The ion radicals were produced by the reaction of the compounds dissolved in 1,2-dimethoxyethane with metallic potassium. Low temperatures were applied for very unstable ions (down to  $-70^{\circ}$ ). The e.p.r.-spectra of the following benzene derivatives were discussed: cumene (Fig 1), cyclohexyl benzene, tert. isobutyl benzene, toluene, ethyl benzene. The spectrum consisted of 5 lines with hyperfine structure and binomial intensity distribution. The observed 5 lines were explained by the inter-

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Investigation of the Spectra of the Electron Paramagnetic Resonance (e.p.r.)  
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action of the unpaired electron with 4 equivalent H-atoms. In the toluene anion (Fig 2) each of the 5 lines is separated into 8 components due to the interaction between the unpaired electron with 3  $\alpha$ -protons and the proton in p-position. In the investigation of the spectra of o-, m-, and p-xylene more detailed results were obtained than had been given in reference 4. The measurement results and the calculated spin densities of the unpaired electron are summarized in table 1. To investigate the transmission of an electron along the chain of the conjugate or saturated bonds the e.p.r.-spectra of the anions of stilbene, azoxybenzene, and dibenzyl were investigated (Fig 3). In stilbene the possibility of a delocalization of the electron along the benzene ring and along the chain of the conjugate double bonds was proved. The spectrum of azoxybenzene



showed that the replacement of the bridge -C=C- by -N=N- does not reduce the mobility of the electron over the entire molecule. Also in dibenzyl the electron does not remain localized to one

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Investigation of the Spectra of the Electron Paramagnetic Resonance (e.p.r.)  
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ring but changes between the two rings with a frequency of the order of magnitude  $10^{-7} - 10^{-8} \text{ cm}^{-1}$ . To check the influence of the heteroatoms on the spin density the e.p.r.-spectra of the pyridine and quinoline anions were investigated. From the pyridine spectrum it is concluded that a spin density differing from zero exists in the N-atom and in the  $\alpha$ -,  $\beta$ - and  $\gamma$ -C-atoms where the  $\alpha$ -,  $\beta$ - and  $\gamma$ -proton are not equivalent. There are 3 figures, 1 table, and 4 references. ✓

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of  
Chemical Physics of the Academy of Sciences, USSR)

SUBMITTED: August 31, 1959

Card 3/3

VOYEVODSKIY, Vladimir V., KONDRAT'YEV, Viktor N.

Institute of Chemical Physics,  
Academy of Sciences USSR.

"Rate Constants for Atomic Exchange Reactions."  
(Scheduled for Morning Session, 6 Sep 60)

paper presented at the Chemical Inst. of Canada, Symposium on Some Fundamental Aspects  
of Atomic Reactions - McGill Univ., Montreal, Canada, 6-7 Sep 60.

reports to be presented at the 2nd Intl Congress on Catalysis, Paris, France, 4-9-Jul '62.

34898

S/081/62/000/003/089/090  
B159/B101

11.2214  
15.8160  
AUTHORS:

Tsvetkov, Yu. D., Lebedev, Ya. S., Voyevodskiy, V. V.

TITLE:

Research on the reactions of free radicals in irradiated teflon

PERIODICAL:

Referativnyy zhurnal. Khimiya, no. 3, 1962, 645, abstract 3R67 (Tr. Tashkentsk. konferentsii po mirn. ispol'zovaniyu atomn. energii. v. 2, Tashkent, AN UzSSR, 1960, 431-440)

TEXT: The electron paramagnetic resonance spectra of the radicals formed on irradiating teflon, and the diffusion of the gases  $H_2$ ,  $O_2$ , NO into the irradiated teflon were studied. At temperatures of 100-200°C a hyperfine splitting due to the interaction of the unpaired electron with 4 fluorine atoms in the gamma position was observed in the spectrum of the radical  $\sim CF_2-CF-CF_2\sim$  (R). The value of this splitting is 3.5 oersts. On lowering the temperature the lines widen; the transition temperature is 135°C, the width of the line 8 Meps. At  $\sim 20^\circ C$  an expansion of the beta-component of the spectrum R is observed combined with a first-order phase Card (1/3)

S/081/62/000/003/089/090  
B159/B101

Research on the reactions ...

transition in the teflon crystal lattice. The diffusion coefficients (D) of O<sub>2</sub>, H<sub>2</sub>, and NO for different temperatures and pressures were determined. A direct dependence of log D on 1/T was found. The effective activation energies of diffusion (kcal/mole) are:

$$E_g(O_2) = 4.6 \pm 0.5; E_g(H_2) = 4.3 \pm 0.5; E_g(NO) = 6.0 \pm 1.$$

D decreases with a lowering of pressure. The kinetics of the reactions of  $\dot{R}$  with O<sub>2</sub>, H<sub>2</sub>, and NO on thin (100-250 μ) teflon films (for the elimination of the effects connected with diffusion) was studied. The

reaction of  $\dot{R} + O_2 \xrightarrow{k_2} RO_2$  proceeds quickly (~ 10 sec). The study of the kinetics of the decomposition  $RO_2 \xrightarrow{k_1} \dot{R} + O_2$  showed that there exist two steps corresponding to the monomolecular decomposition with different k's. The presence of the two steps is dependent on the reactions  $RO_2 \xrightarrow{k_1} \dot{R} + O_2; \dot{R} + O_2 \xrightarrow{k_2} RO_2; O_2 \xrightarrow{k_g} \text{evacuation}$ .  $k_g = \alpha D/d^2$  is the diffusion constant of O<sub>2</sub>. At the initial moment a monomolecular

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Research on the reactions ...

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B159/B101

decomposition takes place with an effective rate constant  $k$ , but at higher degrees of conversion - a quasi-monomolecular reaction with an effective rate constant  $k_{\text{eff}} = k_1 k_2 / k_3 n_0 = k / K n_0$  takes place. Results of the

calculation:  $(k_1 = 10^{-5} v_0 \exp(-20000/RT) \text{ sec}^{-1};$

$k_2 = 10^{-5} Z_0 \exp(-6000/RT) \text{ cm}^{-3}/\text{sec}; \dot{R} + O_2 \xrightleftharpoons[k_3]{k_2} \dot{RO}_2,$

$k = 10^{-23} \exp(14000/RT) \text{ cm}^{-3}$ . The kinetics of the process  $\dot{R} + H_2 \xrightarrow{k_3}$

are described by the quasi-monomolecular law with

$$k_{\text{eff}} = k_3 [H_2]_p = k_3 k_p \frac{(H_2)}{P(H_2)}; k_3 k_p = 50 \exp(-8500/RT) \text{ sec}^{-1}/\text{mm Hg.}$$

The reaction  $\dot{RO}_2 + H_2 \xrightarrow{k_4}$  passes through an intermediate stage - the

decomposition of the peroxide radical.  $E_{\text{act}} = \sim 20 \text{ kcal/mole}$ . The

interaction of  $\dot{R}$  with NO leads to the appearance of the spectrum of a new radical  $\sim CF_2-\dot{C}NO-CF_2 \sim$ . The radical is stable, does not react with  $H_2$  and

$O_2$ , but in the presence of NO decomposes at a temperature  $> 200^\circ$ .

[Abstracter's note: Complete translation.]

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VOYEVOODSKIY, V.V.

Chain concepts in heterogeneous catalysis. Probl. kin. i kat.  
10:369-372 '60. (MIRA 14:5)

1. Institut khimicheskoy fiziki AN SSSR.  
(Catalysis)

S/081/60/000/021/006/018

AC05/AC01

11.6200

Translation from: Referativnyy zhurnal, Khimiya, 1960, No. 21, p. 50, # 83984

AUTHORS: Kazanskiy, V. B., Voyevodskiy, V. V.

TITLE: On the Problem of the Possibility of Chain Mechanisms at the Catalysis on Metals. An Investigation of the Mechanism of Some Catalytic Reactions on Metallic Palladium.

PERIODICAL: Probl. kinetiki i kataliza, 1960, Vol. 10, pp. 398-403

TEXT: The mechanism is studied of three catalytic reactions on metallic Pd at 150 - 300°C: the hydrogen exchange with deuterium; the oxidation of  $H_2$ , and the hydrogenation of  $C_2H_4$ . The reaction mechanism is radical in all the three cases.

Summary of the authors

Translator's note: This is the full translation of the original Russian abstract.

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TIKHOMIROVA, N.N.; MARKIN, M.I.; NIKOLAYEVA, I.V.; VOYEVODSKIY, V.V.

Interaction between molecular oxygen and the free valences of coal.  
Probl. kin. i kat. 10:426-428 '60. (MIRA 14:5)

1. Institut khimicheskoy fiziki AN SSSR.  
(Oxygen) (Charcoal)

S/195/60/001/001/002/007  
B015/B060

AUTHOR: Voyevodskiy, V. V.

TITLE: Application of Electron Paramagnetic Resonance in Chemistry

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 1, pp. 45-54

TEXT: By way of introduction, the author explains the basic principles supporting the method of electron paramagnetic resonance (epr), and gives a survey of the research work conducted in the course of recent years in his laboratory in this field. He supplies results obtained from the investigation of the structure of paramagnetic particles as well as of the negative aromatic ion radicals developing from the electron transition from the alkali metal to the aromatic molecule, as well as of the ions of the general formula  $[\text{Ph}(\text{CH}_2)_n\text{Ph}]^-$  and the radicals arising on the action of ionizing radiation on polymers. The possibilities of epr for the study of elementary reactions of free radicals in the solid phase are explained next, and some results are supplied together with several data of publications. The author finally points out that the method under

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Application of Electron Paramagnetic  
Resonance in Chemistry

S/195,60/001/001/002/007  
E015/B060

discussion is the most promising way of studying free radicals in condensed media, and that it will help to clarify many unsolved problems in the next few years. Ye. K. Zavgyskiy, K. A. Andrianov (INEOS AS USSR), S. P. Solodovnikov, V. M. Chibrikin, N. I. Butnov, F. S. D'yachkovskiy, A. Ye. Shilov, and N. N. Semenov are mentioned in the text. There are 5 figures and 33 references: 22 Soviet, 5 US, 1 Canadian, 5 British, and 1 Italian.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya SO AN SSSR  
(Institute of Chemical Kinetics and Combustion SO AS USSR)

SUBMITTED: December 10, 1959

✓B

Card 2/2

TIKHOMIROVA, N.N.; NIKOLAYEVA, I.V.; VOYEVODSKIY, V.V.

Application of the electronic paramagnetic resonance method to the study of the molecular structure of coals. Zhur. strukt. khim. 1 no.1:99-102 My-Je '60. (MIRA 13:8)

1. Institut khimicheskoy fiziki AN SSSR.  
(Coal) (Paramagnetic resonance and relaxation)

MAZANSKIY, V.B.; PECHERSKAYA, Yu.I.; VOYEVODSKIY, V.V.

Use of the electronic paramagnetic resonance method in the study of  
the crystalline properties of a chromic oxide catalyst. Khim.  
1 kat. 1 no.2:257-259 J1-Ag '60. (MIRA 13:8)

1. Institut khimicheskoy fiziki AN SSSR.  
(Paramagnetic resonance and relaxation)  
(Chromium oxide)

87453

S/195/60/001/002/009/010  
B004/B067

11.1220

AUTHORS: Panfilov, V. N., Tsvetkov, Yu. D., Voyevodskiy, V. V.

TITLE: Detection of Hydrogen Atoms in a Dilute Hydrogen Flame by  
Means of epr

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 2, p. 333

TEXT: In this "Letter to the Editor", the authors report that they detected hydrogen atoms in burning mixtures of  $H_2$  and  $O_2$  at 3 - 20 mm Hg by means of electron paramagnetic resonance. The experiments were made immediately above the lower flash point. After heating to 550 - 600°C,  $H_2$  and  $O_2$  were introduced into a quartz tube through the resonator of the epr spectrometer. A doublet with a g-factor  $\sim 2$  and a splitting of  $\sim 500$  oersteds were recorded. In a stoichiometric mixture of hydrogen and oxygen, the signal power increases by the tenfold if the total pressure is reduced from 16 to 8 mm Hg. This is explained by the quicker flow of the gas mixture at lower pressure. At 8 mm Hg, the signal amplitude increases with increasing hydrogen concentration. At present, the authors

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Detection of Hydrogen Atoms in a Dilute  
Hydrogen Flame by Means of epr

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B004/B067

are studying the dependence of the concentration of hydrogen atoms on temperature, pressure, and the composition of the mixture. They attempt to detect other atoms and radicals. Ye. I. Kondrat'yeva and V. N. Kondrat'yev are mentioned. There are 1 figure and 4 references: 3 Soviet and 1 US.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR)

SUBMITTED: May 23, 1960

Card 2/2

88358

S/195/60/001/004/002/015

B017/B055

5.3832

(2209)

AUTHORS:

Lebedev, Ya. S., Tsvetkov, Yu. D., Voyevodskiy, V. V.

TITLE:

The Origin of the Compensation Effect in Recombination Reactions of Radicals in Irradiated Polymers .

PERIODICAL:

Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 496-502

TEXT: The authors studied the rate constants of the recombination reactions of radicals in hydrocarbon polymerizates, polyvinyl chloride and various Teflon samples. Log  $k^0$  in irradiated polymers was found to be a linear function of the activation energy E. Table 1 gives values of  $k^0$  and E for radical recombination in various polymers. This recombination is generally observed at temperatures around the melting point of the polymer. Within the melting range, the activation energy was found to decrease with an increase in temperature. Basing on the equation  $k = k_0 \exp [-E(T)/RT]$ , the authors calculated E and  $k^0$  from the relations

$$E_{\text{eff}} = E - T \partial E / \partial T \quad (1) \text{ and}$$

$$k_{\text{eff}}^0 = k^0 \exp(-(1/R) \partial E / \partial T) \quad (2).$$

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B017/B055

The Origin of the Compensation Effect in  
Recombination Reactions of Radicals in  
Irradiated Polymers

The true values of  $k^0$  for the recombination of fluoroalkyl radicals in Teflon are shown in Table 2. They are of the order of  $10^{-9}$  -  $10^{-16}$  cm<sup>3</sup>/sec. The true value of E is of the order of 10-20 kcal/mole. The assumed temperature dependence of the activation energy of radical recombination in Teflon is represented graphically in Fig. 2. The anomalous values of  $k^0$  are ascribed not only to the occurrence of phase changes on temperature increase, but also to factors due to condensation of phases. S. Z. Roginskiy and Yu. L. Khait are mentioned. There are 2 figures, 2 tables, and 14 references: 9 Soviet, 4 US, and 1 Polish.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR). Institut khimicheskoy kinetiki i gorennya CO AN SSSR (Institute of Chemical Kinetics and Combustion of SO of the AS USSR)

SUBMITTED: July 27, 1960

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S/195/60/001/004/005/015  
B017/E055

AUTHORS: Kazanskiy, V. B., Pariyskiy, G. B., Voyevodskiy, V. V.

TITLE: A Study on the Properties of Hydrogen Atoms Adsorbed on Silica Gel Surfaces by Applying Electron Paramagnetic Resonance

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 539-541

TEXT: R. Livingston, H. Zeldes, E. H. Taylor (Ref. 1) and N. N. Bubnov, V. V. Voyevodskiy, L. S. Polyak and Yu. D. Tsvetkov found that under the influence of  $\gamma$ -radiation at liquid nitrogen temperature hydrogen atoms, detectable by the EPR method, are formed from adsorbed water molecules or OH groups on the surfaces of glass and silica gel. The properties of the hydrogen atoms adsorbed on the surface of silica gel were studied in the present publication.  $\text{Co}^{60}$  was used as source of radiation. The EPR spectra were taken at liquid nitrogen temperature on a spectrometer with a high-frequency magnetic field. The spectra of the irradiated silica gel are represented graphically in a figure. The removal of hydrogen atoms from the silica gel surface in presence of ethylene was investigated, and

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A Study on the Properties of Hydrogen Atoms  
Adsorbed on Silica Gel Surfaces by Applying  
Electron Paramagnetic Resonance

S/195/60/001/004/005/015  
B017/B055

it was found that the desorption rate of hydrogen atoms in presence of  
ethylene exceeds the desorption rate in vacuum by a factor of thirty.  
Hydrogen atoms adsorbed at -100 to -150°C react with ethylene and oxygen.  
There are 1 figure and 3 references: 2 Soviet and 1 British.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical  
Physics of the AS USSR)

SUBMITTED: August 2, 1960

Card 2/2

21.6000

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20544  
S/051/60/008/06/010/024  
E201/E691

AUTHORS: Lebedev, Ya.S., Tavetkov, Yu.D., and Voyevodskiy, V.V.

TITLE: The Electron Paramagnetic Resonance Spectra of Fluoroalkyl and Nitrosofluoroalkyl Radicals in Irradiated Teflon

PERIODICAL: Optika i spektroskopiya, 1960, Vol 8, Nr 6, pp 811-814 (USSR)

ABSTRACT: The authors describe their results obtained in an investigation of electron paramagnetic resonance (EPR) spectra of fluoroalkyl and nitrosofluoroalkyl radicals in irradiated teflon at temperatures up to 300°C. An EPR spectrometer with high-frequency (300 kc/s) magnetic-field modulation, described earlier (Ref 4), was used. The samples were heated by blowing hot air around them. The EPR spectrum of the fluoroalkyl radical exhibited additional hyperfine splitting of 3.5 oersted at high temperatures. This splitting was due to the interaction of the unpaired electron with fluorine atoms in the  $\gamma$ -position (Fig 1 shows this at 250°C). These  $\gamma$ -components were broadened on cooling (Fig 2) so that at room temperature they could no longer be resolved. Fig 3 shows that on further lowering of temperature to about 16°C the  $\beta$ -components broaden as well and finally below 0°C the hyperfine splitting due to  $\alpha$ - and  $\beta$ -atoms of fluorine

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S/051/60/008/06/010/024  
E201/E691

The Electron Paramagnetic Resonance Spectra of Fluoroalkyl and Nitrofluoroalkyl Radicals in Irradiated Teflon

disappears completely. Gordy (Ref 2) reported that the EPR spectrum of fluoroalkyl radical disappeared on interaction with NO. The present authors found that simultaneously with the disappearance of the original fluoroalkyl spectra a new complex EPR spectrum appears (Fig 4). This new spectrum is ascribed to the nitrofluoroalkyl radical and its profile at 150°C (Fig 4a) agrees with theoretical predictions (Fig 4b). Splittings in the EPR spectrum of nitrofluoroalkyl suggest that the unpaired electron is localized mainly at the nitrogen nucleus. The paper ends with a short discussion of the results obtained and comparison with other published work. There are 5 figures and 11 references, of which 3 are Soviet and 8 English.

SUBMITTED: September 21, 1959

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5.3100  
5.4500(B)

S/020/60/130/06/031/059  
B004/B007

AUTHORS:

Chkheidze, I. I., Molin, Yu. N.,  
Buben, N. Ya., Voyevodskiy, V. V.,

Corresponding Member AS USSR

TITLE:

The E.P.R.-Spectra and the Kinetics of the Accumulations of  
Radicals in the Radiolysis of Some Aromatic Compounds

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 6, pp 1291 - 1293  
(USSR)

ABSTRACT:

It was the aim of the present paper to determine the nature of the radicals formed in the radiolytical decomposition of aromatic hydrocarbons, as well as to investigate the influence exerted by structure upon the yield of radicals. The electron paramagnetic resonance (e.p.r.) - spectra of the radicals were recorded which are formed under the influence of fast electrons (1.6 Mev), and the kinetics of their accumulation was measured. Irradiation was carried out at -124 and at +33°. Chemically pure benzene was used. The other compounds: diphenyl, p-ditolyl, o-ditolyl, m-terphenyl, and p-terphenyl were supplied by the laboratory of K. P. Lavrovskiy of the Institut neftekhimicheskogo sinteza (Institute of Petroleum-chemical Synthesis). Figure 1 shows the e.p.r. spectra at -124°. The e.p.r. spectrum

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The E.P.R.-Spectra and the Kinetics of the  
Accumulations of Radicals in the Radiolysis of  
Some Aromatic Compounds

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B004/B007

of benzene shows a well resolved triplet, the central component of which is, however, considerably more intense than corresponds to the binomial law. This is explained by the superposition of the triplet and a single line. The triplet is ascribed to the radical  $C_6H_5$ , the unpaired electron of which

enters into interaction with the adjacent H-atoms. The low yield in molecular hydrogen leads to the conclusion that the H-atoms mostly join the benzene ring, forming the radical  $C_6H_7$ , 

which produces the single line. The superfine structure of the e.p.r. spectrum of benzene becomes more distinct with rising temperature. This is explained by the quickening of the inhibited rotation round the axis of the sixth order, the existence of which was detected in the course of the investigation of nuclear resonance. The components of the e.p.r. spectra of terphenyls and ditolyls are also triplets, but they are not so distinctly resolved. These spectra are explained by the detachment of hydrogen atoms or  $CH_3$ -groups in paraposition to

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The E.P.R.-Spectra and the Kinetics of the  
Accumulations of Radicals in the Radiolysis of  
Some Aromatic Compounds

the phenyl substituent, where the detached H or CH<sub>3</sub> again joins  
on the benzene ring, similar to the case of the radical C<sub>6</sub>H<sub>7</sub>.

The low resolution of the polyphenyl spectra is explained by  
delocalization of the unpaired electron. Table 1 shows the  
radical yields, figure 2, the kinetics of the accumulation of  
radicals. The low radical yields of ditolyls and terphenyls as  
against benzene agree with published data on the greater sta-  
bility of polyphenyls (Ref 9). As regards the isomer yields,  
the differences found are within the error limits. The authors  
thank A. M. Brodskiy and V. B. Titov for the polyphenyls placed  
at their disposal and for discussing the results obtained, and  
they further thank V. N. Shamshev for taking part in the ex-  
periments. There are 2 figures, 1 table, and 13 references,  
4 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of  
Chemical Physics of the Academy of Sciences, USSR). Institut  
khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR  
Card 3/3 (Inst Chem. Kinetics & Combustion, Siberian Dept, AS USSR)

Boyevodskiy, V.V.

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Case 2/3

Case 2/3

1500-111031

**SECRET**

November 4, 1953

[illegible][illegible]

S/020/60/132/04/36/064  
B004/B007

AUTHORS:

Azatyan, V. V., Vovkovodskiy, V. V., Corresponding Member of  
the AS USSR, Nalbandyan, A. B.

TITLE:

Determination of the Rate Constant of the Reaction of Atomic  
Oxygen With Molecular Hydrogen

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4, PP. 864-867

TEXT: For the reaction  $O + H_2 = OH + H$  (III) the rate constant  $k_{III}$  was determined by measuring the lower flash point of  $CO + O_2$  mixtures in the case of various additions of  $H_2$ . On the basis of the reaction mechanism suggested in publications, among them those by V. N. Kondrat'yev (Ref. 6), N. S. Yenikolopyan and A. B. Nalbandyan (Ref. 7), the authors derive equation (1) for the flash point and equation (3) for the dependence between the total pressure  $P$  and the partial pressures  $P_{O_2}$  and  $P_{H_2}$ , and finally equation (8) for  $\log (\tan \alpha / bT^{2.5})$ , where  $\tan \alpha$  and the factor  $b$

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Voyevodskiy, V. V.

S/020/60/133/03/12/013  
B004/B056 82276

5.383/

AUTHORS:

Yakovleva, Ye. A., Petrov, E. S., Solodovnikov, S. P.,  
Voyevodskiy, V. V., Corresponding Member AS USSR,  
Shatenshteyn, A. I.

TITLE:

The Influence of Metal and Solvent Upon the Formation of  
Aromatic Anion Radicals as Initiators of Polymerization ↑

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 3,  
pp. 645 - 648

TEXT: In the introduction, the authors give a survey of publications concerning investigations of anion radicals (AR) formed by the transition of an electron from alkali metal to an organic molecule. They then describe their own investigations of the formation of the AR of benzene and toluene. The following solvents were used: 1,2-dimethoxyethane (DME), 1,2-methoxy-ethoxy-ethane (MEE), 1,2-diethoxyethane (DEE), tetrahydrofuran (THF), and 1,3-dioxane (DO). The AR were detected by means of electron paramagnetic resonance. The frozen solvent with the aromatic compound was placed in an evacuated ampoule, on the walls of which potassium

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The Influence of Metal and Solvent Upon the  
Formation of Aromatic Anion Radicals as Initiators  
of Polymerization

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had precipitated. Experiments carried out with benzene (0.4 mole in 1 l of solution at  $-30^{\circ}\text{C}$ ) with an addition of K and DME produced an AR concentration that was 4 to 5 times higher than with DEE. With Na and DEE the AR concentration was lower by at least 2 orders of magnitude. Parallel experiments carried out with Li and Na in DEE at  $-70^{\circ}\text{C}$  gave a considerably higher AR concentration for Li. Experiments with toluene supplied the data given in Table 1. The relative concentration of AR was determined, the AR concentration in DME being set equal to 100. The experimental results led to the following conclusions: 1) Benzene forms AR with Li, Na, and K. Potassium-anion radicals formed in all solvents used; 2) substitution of the methyl group of ether by the ethyl group decreased the stability of AR as a result of steric hindrance. Stability decreases in the following order: DME, MEE, DEE. 3) The sodium compound of aromatic hydrocarbon does not form so easily as the K- and Li-compounds. - The initiation of the polymerization of styrene was investigated by means of benzene potassium in DME, MEE, and DEE. The electron paramagnetic resonance spectrum of these solutions showed a narrow singlet (Fig. 1). In the initiation of the polymerization by means of a solution of K in DME without benzene

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of Polymerization

S/020/60/133/03/12/013  
B004/B056 82276

(-50 - -80°C) a quintuplet (Fig. 2) was observed. This was explained by transition of an electron into the aromatic ring of polystyrene. The polymers had a molecular weight of from 350,000 to 600,000. The authors are continuing their investigations. They thank Ye. A. Kovrizhnykh for his help rendered, A. K. Rusanov for the spectrum analysis of potassium, which was carried out in his laboratory, and Yu. P. Vyrskiy for determining the molecular weight of the polymers. There are 2 figures, 1 table, and 16 references: 4 Soviet, 9 American, 2 German, and 1 Japanese.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute im. L. Ya. Karpov). Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR)

SUBMITTED: March 22, 1960

Card 3/3

83566

S/020/60/134/001/019/021  
B004/B060

54500

AUTHORS:

Shelimov, B. N., Bubnov, N. N., Fok, N. V.,  
Voyevodskiy, V. V., Corresponding Member AS USSR

TITLE:

Detection of Hydrogen Atoms in the Phototransfer Reactions  
of the Electron 2/

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 1,  
pp. 145 - 148

TEXT: The authors proceed from the photochemical reaction in the aqueous medium:  $M + H_2O + h\nu \rightarrow M^+ + OH^- + H(1)$ , where M may be metal ions of variable valency, or anions. The formation of hydrogen atoms in this reaction had been hitherto proved indirectly only. The authors wanted to give direct evidence of H-atoms by means of electric paramagnetic resonance (epr). Because of the strong reactivity and mobility of the H-atoms, investigations were conducted at 77°K in aqueous solutions of  $H_2SO_4$  or  $H_3PO_4$  (in concentrations between 40 and 96%), which contained small quantities of  $FeSO_4$  or KI. The samples were irradiated for 1 hour

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83566

S/020/60/134/001/019/021  
B004/B060

Detection of Hydrogen Atoms in the  
Phototransfer Reactions of the Electron

with the ultraviolet light of a ПPK-7 (PRK-7) mercury vapor lamp. The epr signals were recorded by means of a previously described (Ref. 7) epr spectrometer. It was possible to give evidence of the H-doublet. To check the correctness of reaction (1) definitely, experiments were made in solutions which contained heavy water. As is shown by Fig. 1, the D-triplet was observed besides the H-doublet. Further experiments were conducted in the system  $C_6H_6 - H_2O - H_2SO_4$ . Here as well (Fig. 2) the H-doublet occurred. The central part of this spectrum, the quadruplet shown in Fig. 3, could not be explained yet, but it might be due to a paramagnetic particle whose free valency is localized on the aromatic ring. Weaker components were detected in the epr spectrum of the H-atom (Fig. 4), which are ascribed to the spin reversal of protons surrounding the H-atom. While the H-lines were strongly saturated in the experiments with benzene, saturation did not take place in the presence of  $Fe^{2+}$  due to higher concentration of the paramagnetic ions of a short relaxation time. The study of saturation and intensity distribution between the main and secondary lines in the epr spectrum of  $H^\bullet$  may serve to clarify specific features of its weak interaction

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83566

Detection of Hydrogen Atoms in the  
Phototransfer Reactions of the Electron

S/020/60/134/001/019/021  
B004/B060

with adjacent molecules, and also to establish the distance between  
H<sup>+</sup>-atoms and primary particles releasing an electron under the action  
of light. There are 4 figures and 12 references: 3 Soviet, 8 US, and  
2 British.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova  
(Moscow State University imeni M.V. Lomonosov). Institut  
khimicheskoy kinetiki i gorenija Sibirskogo otdeleniya  
Akademii nauk SSSR (Institute of Chemical Kinetics and  
Combustion of the Siberian Branch of the Academy of  
Sciences, USSR)

SUBMITTED: April 27, 1960

Card 3/3

24-7700  
AUTHORS:

1043, 1136, 1151

86049  
S/020/60/135/003/035/039  
B004/B060

Kachanova, Zh. P., Voyevodskiy, V. V., Corresponding  
Member of the AS USSR, and Purnali, A. P.

TITLE:

Electrical Conductivity of MnO<sub>2</sub> Semiconductors<sup>1</sup> in the  
Course of CO Oxidation<sup>2</sup>

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3,  
pp. 648 - 650

TEXT: The authors attempted to find out whether the electron properties of a semiconductor catalyst undergo any changes during reaction processes. The study was conducted on the catalysis of CO oxidation by means of MnO<sub>2</sub>. A continuous-operation apparatus was used for the purpose. The resulting CO<sub>2</sub> was frozen out, and the electrical conductivity of MnO<sub>2</sub> was measured during the process of catalysis. The measurement of the Hall effect and thermo-emf made by T. I. Kolomenskaya at the Fizicheskiy institut AN SSSR (Institute of Physics of the AS USSR) showed that MnO<sub>2</sub> is an n-type semiconductor. Two stages were distinguished in the training of the catalyst. The catalytic activity is low at the beginning, but

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86049

Electrical Conductivity of  $MnO_2$  Semi-conductors in the Course of CO Oxidation

S/020/60/135/003/035/039  
B004/B060

increases with each experiment. A striking feature is the fact that the oxygen contained in the reaction mixture has no effect on electrical conductivity, while adsorbed oxygen reduces the conductivity. Thus, no adsorption of  $O_2$  takes place with CO oxidation. In the second stage, the catalyst has attained a constant catalytic activity. At the same time, conductivity during the catalytic reaction is considerably higher than in vacuum. This conductivity change  $\Delta\sigma$  is reversible. It appears as soon as the catalyst comes into contact with the reaction mixture, and disappears when the reaction mixture is rapidly sucked off. Thus,  $MnO_2$  is in the state of electron excitation during the catalytic process, i.e., it is not in the state of equilibrium in terms of thermodynamics. Between the rate of the catalytic process and the degree of deviation from equilibrium, a linear relationship was found for all conditions examined. The authors thank B. P. Bruns for having supplied the  $MnO_2$  specimens. There are 3 figures and 14 Soviet references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 18, 1960

Card 2/2

VOYEVODSKIY, Vladislav V., KAZANSKIY, V. B. and PARIYSKIY, G. B.

"Radiation induced surface reactions in silicagel."

report to be submitted for the Faraday Society, General Discussion  
on Radiation Effects in Inorganic Solids, Gif-sur-Yvette (Seine-et-Oise), France,  
11-12 Apr 1961.

Inst. of Chemical Physics, Acad. Sci. USSR, Moscow

S/058/62/000/002/008/053  
A058/A101

AUTHOR: Voyevodskiy, V. V.

TITLE: Application of electron paramagnetic resonance to the investigation of free radicals in the liquid phase

PERIODICAL: Referativnyy zhurnal, Fizika, no. 2, 1962, 46-47, abstract 2V375 ("Tr. po khimii i khim. tekhnol.", Gor'kiy, 1961, no. 1, 52-57)

TEXT: The application of electron paramagnetic resonance to the study of free radicals in the liquid phase is summarized. In investigating the structure and reactions of stable free radicals with sufficiently high stationary concentrations, electron paramagnetic resonance as compared with the usual method of magnetic balance, yields a gain in sensitivity amounting to 3-4 orders of magnitude and enables one to determine details of structure in paramagnetic particles. The author points out the effectiveness of applying electron paramagnetic resonance to the study of the mechanism of some complex liquid-phase processes of polymerization and of photochemical reactions. With the exception of a few cases, however, the application of electron paramagnetic resonance to the investigation of the kinetics of radical processes is at present limited by the

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S/058/62/000/002/002/053  
A058/A101

Application of electron paramagnetic ...

sensitivity of the method (stationary concentrations of free radicals greater than  $10^4$  l/cm<sup>3</sup> are prerequisite).

E. Kharakhash'yan

[Abstracter's note: Complete translation]

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VOYEVODSKIY, V. V.

33101  
S/638/61/001/002/026/056  
2104/2133

54600

AUTHORS:

Molin, Yu. N., Chkheidze, I. I., Petrov, A. A., Buben, N. Ya.,  
Voyevodskiy, V. V.

TITLE:

Investigation of energy transfer processes during the  
radiolysis of congealed hydrocarbons, by the paramagnetic  
electron resonance method

SOURCE:

Tashkentakaya konferentsiya po mirnoy ispol'zovaniyu  
atomnoy energii. Tashkent, 1959. Trudy, v. 1. Tashkent,  
1961, 178 - 181

TEXT: The following compounds were investigated: (I) 1,1-dicyclohexyl  
dodecane; (II) 1,1-diphenyl dodecane; (III) 1-phenyl 1-cyclohexyl  
dodecane. The energy transfer during radiolysis was determined by means  
of paramagnetic electron resonance, and from the total radiation yield.  
Paramagnetic electron resonance spectra were taken of compounds I - III,  
and of benzene and cyclohexane. The substances were irradiated with  
1.6-Mev electrons at -120°C. The spectra were taken during irradiation  
with electrons. The cyclohexyl radical,  $\text{C}_6\text{H}_{10}^\bullet$ , was primarily formed when

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33101  
5/638/61/001/000/026/056  
B104/B138

Investigation of energy transfer...

irradiating compound I. Radicals are also formed by breaking C-H bonds. The spectra of the irradiated compounds II and III are equal, and similar to that of benzene. The radicals are formed: the first by the removal of an H atom from the benzene ring, the second by addition of an H atom to a benzene ring. When irradiated a mixture of compounds I and II, radicals are mainly formed from irradiation of compound II. In irradiation of compounds II and III, it is mainly the bonds in the benzene ring which are broken. In compound I, the first rupture of C-H bonds may be accompanied by a reaction of the H atom, which then permits the formation of radicals. The production of radicals is linearly dependant on irradiation. The yield of radicals in compounds II and III is one order of magnitude smaller than that of compound I. The nearly equal yields of radicals of compounds II and III prove that the energy is transferred to the benzene ring. The yield of radicals in compounds II and III is almost three times that in benzene. This decrease in stability is explained by rupture of the symmetry of the benzene ring. There are 3 figures, 1 table, and 9 references; 4 Soviet and 5 non-Soviet. The four most recent references to English-language publications read as follows: Smaller B., Matheson M. S., J. Chem. Phys., 28, 1169, 1958; Alger R. S.

Card 2/3

33101

S/638/61/001/CCO/026/056  
B104/B138

Investigation of energy transfer...

Anderson T. H., Webb L. A. J. Chem. Phys., 30, 695, 1959; Rad. Res. 3,  
1, 1955; Andrew E. R., Eades R. G. Proc. Roy. Soc., 216A, 398, 1953.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya Sibirskogo  
otdeleniya AN SSSR (Institute of Chemical Kinetics and  
Burning of the Siberian Department AS USSR)

Card 3/3

VOYEVODSKIY, V.V.

"Mechanism of hydrocarbon oxidation in the gas phase" by V.IA.  
Shtern. Reviewed by V.V.Voevodskii. Neftekhimiia 1 no.1:124-125  
Ja-F '51. (MIRA 15:2)  
(Hydrocarbons) (Oxidation) (Shtern, V.IA.)

20988

S/195/61/002/001/002/006  
B101/B216

5.4500(B)

AUTHOR: Voyevodskiy, V. V.  
TITLE: The mechanism of radiolysis of water  
PERIODICAL: Kinetika i kataliz, v. 2, no. 1, 1961, 14-20

TEXT: The author treats the problem of the extraordinarily high effect of minute impurities on the radiolysis of water. He discusses the diffusion theory developed by H. Fricke (Ref. 1: Cold Spring Harbour Symposium on Quantitative Biology, 11, 241, 1934), the radical theory of J. Weiss (Ref. 2: Nature, 153, 748, 1944), and the corrections proposed in this connection by A. O. Allen (Ref. 5, see below), F. S. Dainton, H. S. Sutton (Ref. 4, see below) and K. J. Laidler (Ref. 6, see below). Then, the author discloses his views on a migration theory. Experiments on the radiolysis of frozen 1,1-diphenyl-n-dodecane and 1,1-dicyclohexyl-n-dodecane performed at the author's institute form the experimental basis of this theory. In these experiments, the migration of energy of primary excitation could be directly verified by epr spectra. A similar work by H. T. J. Chilton, G. Porter, E. E. Strachan (Ref. 10: Informal Discussion,

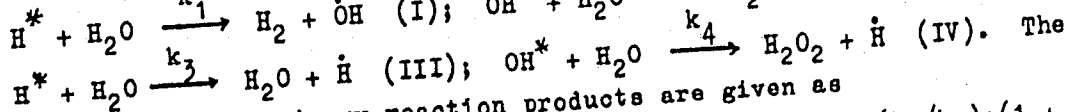
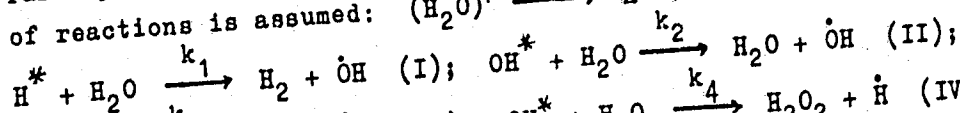
Card 1/4

20988

S/195/61/002/001/002/006  
B101/B216

The mechanism of radiolysis of water

Faraday Soc., Sheffield, 1958, 11) is mentioned. The following sequence of  
of reactions is assumed:  $(H_2O)^* \xrightarrow{(O)} H^* + OH^* (0);$



yields of these primary reaction products are given as

$$G_H = G_0 \left[ (1 + k_1/k_3)^{-1} + (1 + k_2/k_4)^{-1} \right], \quad (9); G_{H_2} = G_0 (k_1/k_3) \cdot (1 +$$

$$+ k_1/k_3)^{-1} \quad (10); G_{H_2O_2} = G_0 (1 + k_2/k_4)^{-1} \quad (11); G_{OH} = G_0 \left[ (k_1/k_3) \cdot (1 +$$

$$+ k_1/k_3)^{-1} + (k_2/k_4) \cdot (1 + k_2/k_4)^{-1} \right] = 2G_0 - G_H. \quad \text{It is concluded that}$$

(1)  $G_{H_2}/(G_H - G_{H_2O_2}) = k_1/k_3$  must be smaller than unity, and (2)

$(G_H + G_{H_2})/G_{H_2O_2} = 2 + k_2/k_4$  must be larger than 3. From a work by

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20988

S/195/61/002/001/002/006  
B101/B216

The mechanism of radiolysis of water

A. O. Allen, H. A. Schwarz (Ref. 15: Proceedings of the 2nd International Conference on the Peaceful Use of Atomic Energy, Geneva, Pergamon Press, Lond., P/1403, 4, 1958, 30) the author took the following values:  
 $G_H = 2.8$ ;  $G_{H_2} = 0.42$ ;  $G_{H_2O_2} = 0.71$ , and obtained  $k_1/k_3 \approx 0.21$ ;

$k_2/k_4 \approx 4.6$ . Thus, the scheme suggested gives quantitative indications as to the relations between the quantities determining the direction of primary decomposition of water. The author invites discussion of this reaction scheme, and suggests that its validity be tested on various problems of radiolysis of water and aqueous solutions. Mention is made of M. A. Proskurnin, V. G. Levich, and R. R. Dogonadze. This paper was read at the Second All-Union Conference on Radiation Chemistry, Moscow, October 1960. There are 15 references: 4 Soviet-bloc and 9 non-Soviet-bloc. The 3 references to English-language publications read as follows: F. S. Dainton, H. C. Sutton, Trans. Faraday Soc., 49, 1011, 1955; A. O. Allen, Rad. Res., 1, 85, 1954; K. J. Laidler, The Chemical Kinetics of Excited States, Oxford, 1955.

Card 3/4

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S/195/61/002/001/002/006  
B101/B216

The mechanism of radiolysis of water

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of  
Chemical Physics of the AS USSR)

SUBMITTED: October 15, 1960

Card 4/4

5.4300

1273, 1320 2060 1138, 1160

21768  
S/195/61/002/002/004  
B101/B208

AUTHORS:

Molin, Yu. N., Chkheidze, I. I., Buben, N. Ya., Voyevodskiy, V. V.

TITLE:

Study of energy transfer to aromatic groups by epr in the radiolysis of organic compounds

PERIODICAL:

Kinetika i kataliz, v. 2, no. 2, 1961, 192-196

TEXT: In Ref. 1 (Dokl. AN SSSR, 131, 125, 1960) the authors have shown by means of epr that in the radiolysis of phenyl-substituted saturated hydrocarbons an energy transfer takes place from the saturated groups to the benzene ring. The present paper gives a preliminary survey on studies carried out on different molecules of the A-D type (A = aromatic energy acceptor, D = radiation-unstable substituent). The compounds studied were synthesized in the laboratory of A. D. Petrov, Corresponding Member AS USSR. Measurements were made on an ЭПР-2 (EPR-2) apparatus of the first association, by means of 1.6 Mev electrons. The radiochemical yield G of radicals was determined from the linear initial section of the accumulation curve. The accumulation of radicals was linear up to a concentration  $\sim 10^{20} \text{ g}^{-1}$ .

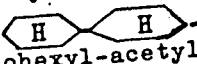
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S/195/61/002/002/004  
B101/B208

Study of ...

The integral dose was varied from 10 to 200 Mrad, the dose rate from 0.03-0.3 Mrad/sec. Irradiation and measurement were performed at 90-160°K. In some cases, "foreign" epr signals were observed at lower doses, whose intensity was  $\sim 10^{18}$  spins/g. This is exemplified in Fig. 1 on the epr spectrum and the accumulation curve for o-ditolyl. The foreign signals are attributed to impurities. Their appearance may give rise to considerable discrepancy of the experimental data at different doses. The G values of several compounds are given in a table:

Compound	G, 1/100 ev	
Paraffin, polyethylene, cyclohexane,	~5	
compounds of the class  -R	~4	
Cyclohexyl-hexine, cyclohexyl-acetylene	0.23	0.04
benzene	0.09	
phenyl acetylene	0.045	
diphenyl	0.045	
p-terphenyl		

The following conclusions may be drawn: 1) For saturated hydrocarbons and

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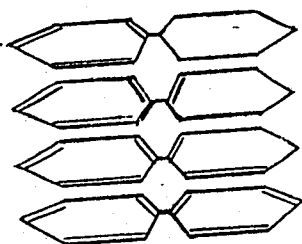
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B101/B208

Study of ...

hydrocarbons with a double or triple bond the G values differ little and amount to several radicals per 100 ev of energy absorbed. 2) In aromatic hydrocarbons without saturated substituents G is by 1-2 orders of magnitude smaller than in saturated hydrocarbons. 3) The radiation stability of aromatic hydrocarbons increases with the degree of conjunction and seems to approach a limit. This also results from G for the following series:

Compound



G, 1/100 ev

0.55

0.2

0.07

0.045

The difference of G for aromatic and non-aromatic hydrocarbons permits to



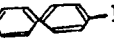
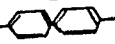
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B101/B208

Study of ...

estimate the probability of energy transfer in a complicated AD molecule by measuring the  $G_{AD}$ :  $G_{AD} = G_A(\gamma_A + \alpha\gamma_D) + G_D\gamma_D(1 - \alpha)$  (1), where  $G_A$ ,  $G_D$  is the radiation yield of the radicals from the groups A and D,  $\gamma_A$ ,  $\gamma_D$  are the electron parts of these groups,  $\alpha$  the probability of energy transfer from D to A. At  $\alpha = 0$ , additivity occurs:  $G = G_A\gamma_A + G_D\gamma_D$  (2). The probability of energy transfer is calculated from equation (1):  $\alpha = [(G_A\gamma_A + G_D\gamma_D) - G_{AD}] / (G_D - G_A)\gamma_D$  (3). The following classes of compounds were studied:

I. -R, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, cycl-C<sub>6</sub>H<sub>11</sub>; II. -(CH<sub>2</sub>)<sub>n</sub>SiR<sub>3</sub>; R = CH<sub>3</sub>, n = 0, 1, 2, 3; R = C<sub>2</sub>H<sub>5</sub>, n = 0 and 3. III: -R and R' -R, where R, R' denotes a saturated hydrocarbon chain, a chain with a double bond, or with a CO group (number of C atoms up to 8).  $\alpha$ , calculated by Eq. (3) was between 0.65-0.95. No systematic difference of  $\alpha$  was found for the three classes. Fig. 2 shows their epr spectra. Classes I and II (Figs. 26, 28) mainly show lines corresponding to a cleavage of C-H bonds in the benzene ring. Class III (Fig. 21) shows a more complicated spectrum. In the case of long chains of

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Study of ...

the substituent lines predominate which are assigned to a bond cleavage in the substituent.. This may be explained by the fact that at  $\alpha < 1$  a C-H bond cleavage in the ring becomes less probable than in the radical in spite of energy transfer, owing to a larger stability of the diphenyl group. The small difference between the spectra of I and II and that of benzene (Fig. 2a) is presumably due to the fact that a) the broad spectra of the alkyl radicals form only a background, or b) the stability of the  $C_6H_6$  ring decreases on substitution. This problem has still to be clarified. The authors express their gratitude to Ye. D. Kaplan, Ye. A. Chernyshev, V. F. Mironovich, of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry, AS USSR) for the synthesis of compounds, to G. K. Voronova for her cooperation. There are 2 figures, 1 table, and 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The reference to English language publication reads as follows: N. K. Bridge, Nature, 185, 30, 1960.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR) Institut khimicheskoy kinetiki i gorennya SO AN SSSR (Institute of Chemical Kinetics and Burning of the Siberian Department, AS USSR)

Card 5/7

MOLIN, Yu.N.; CHKHEIDZE, I.I.; BUBEN, N.Ya.; VOYEVODSKIY, V.V.

Electron paramagnetic resonance spectra of irradiated dicarboxylic acids. Zhur.strukt.khim. 2 no.3:293-300 My-Je '61. (MIRA 15:1)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy kinetiki i gorennya Sibirskogo otdeleniya AN SSSR.  
(Acids, Organic--Spectra)

30918

S/195/61/002/003/003/009  
E111/E130

11.6200(also 3619)

AUTHORS: Azatyan, V.V., Voyevodskiy, V.V., and Nalbandyan, A.B.

TITLE: Determination of the rate constant for the reaction of atomic oxygen with molecular hydrogen

PERIODICAL: Kinetika i kataliz, v.2, no.3, 1961, 340-349

TEXT: The reaction of atomic oxygen with molecular hydrogen to give the hydroxyl radical and atomic hydrogen often occurs in the oxidation process, sometimes playing an important part. This reaction has not been sufficiently studied and there are no reliable published data on its rate constant. The authors have used a new method for making this determination. The velocity constants were measured by observing the flame boundaries in the burning of carbon monoxide in the presence of varying small concentrations of hydrogen. A conventional type of reaction apparatus was used, but it was found that the quantities reacting could be increased by coating the walls of the reaction chamber. NaCl and KCl coatings gave a several-fold increase, but MgO gave an increase of about fifty times, and therefore all work was done with magnesia-coated chambers, since much sharper flame-edge

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S/195/61/002/003/003/009  
E111/E130

Determination of the reaction velocity..

resolution could be obtained. The reaction oven temperature was controlled to  $\pm 0.2$  °C. Fig.2 shows values of the ignition limits as functions of temperature (570-660 °C) for a mixture of  $2H_2 + O_2$  (curve 1) and mixtures of  $2CO + O_2$  with 5.26, 3.06 and 1.01%  $H_2$  (curves 2, 3 and 4 respectively) for the 55-mm diameter vessel; results for  $2CO + O_2$  mixtures with 7.95, 4.15, 2.04 and 0.695%  $H_2$  are shown by curves 1, 2, 3 and 4 respectively in Fig.6. The work showed that the main carriers in the chain are OH and O, that the main reaction in the recombination of O and H atoms is their destruction on the vessel walls, and that the heterogeneous chain-breaking occurs in the diffusion region. The reaction temperature was varied between 570 and 660 °C and the hydrogen content of the mixtures from 0.7% to 8%. Because of the sharp edge definition possible, the reaction occurred under conditions of:

$$ed/\lambda \gg 1,$$

where  $e$  is the effectiveness of recombination of active centers at the surface,  $d$  the diameter of the vessel, and  $\lambda$  the mean free path (as verified by addition of inert nitrogen gas).

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Determination of the reaction ...

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S/195/61/002/003/003/009  
E111/E130

Confirmation of the correctness of the approach used was obtained by independent calculations using diffusion in coefficient values. The rate-constant values for the reaction  $O + H_2 = OH + H$  was found to be  $1.11 \times 10^{-10} e^{-11700/RT}$  and for  $H + O_2 = OH + O$ ,  $1.30 \times 10^{-10} e^{-15900/RT}$

$cm^3, molecule^{-1}, sec^{-1}$ .

L.I. Abramenko, R.V. Lorentso, V.N. Kondratyev and N.S. Yenikolopyan are mentioned for their contributions in this field. There are 8 figures, 3 tables and 30 references: 13 Soviet-bloc, 1 Russian translation from non-Soviet publication, 1 English translation from a Soviet author, and 15 non-Soviet-bloc. The four most recent English language references read as follows:  
Ref.20: D.R. Warren, Trans. Faraday Soc., v.53, 199, 1957.  
Ref.21: D.R. Warren, Trans. Faraday Soc., v.53, 206, 1957.  
Ref.22: I.G. Greaves, J.W. Linnet, Trans. Faraday Soc., v.54, 1323, 1958.  
Ref.29: P. Gray, Trans. Faraday Soc., v.55, 408, 1959.

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Determination of the reaction velocity.. 30918  
S/195/61/002/003/003/009  
E111/E130

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR  
(Institute of Chemical Physics, AS USSR)

SUBMITTED: February 21, 1961

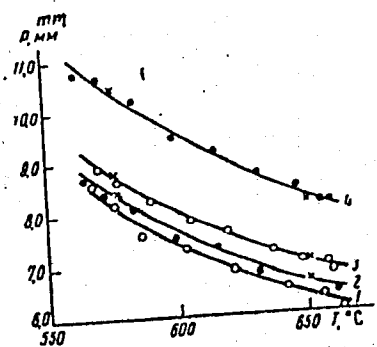


Fig. 2

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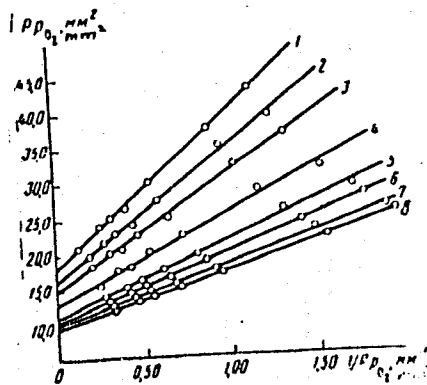


Fig. 6

KAZANSKIY, V.B.; YEZHKOVA, Z.I.; LYUBARSKIY, A.G.; VOYEVODSKIY, V.V.;  
IOFFE, I.I.

Electron paramagnetic resonance study of the structure of  
vanadium-molybdenum oxide catalysts. Kin. i kat. 2 no.6:862-866  
N-D '61. (MIRA 14:12)

1. Institut khimicheskoy fiziki AN SSSR i Institut organicheskikh  
poluproduktov i krasiteley imeni K.Ye. Voroshilova.  
(Catalysts--Spectra)

S/190/61/003/006/013/019  
B110/B208

11.2214 dno 2209  
AUTHORS:

Tsvetkov, Yu. D., Lebedev, Ya. S., Voyevodskiy, V. V.

TITLE:

Study of free radical reactions. III. Recombination of fluoroalkyl and peroxide radicals

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 882-890

TEXT: The purpose of the present paper is the investigation of the recombination reactions of fluoroalkyl and peroxide radicals under exclusion of oxygen diffusion. The dependence of the radical recombination on the ratio of the amorphous and crystalline phase was studied on Teflon with different degree of crystallinity. Teflon samples in the form of films or chips were irradiated by a  $\gamma\text{Co}^{60}$  radiation source at  $\sim 60$  Mrad. The free radical concentration is in this case  $\sim 10^{18}$   $1/\text{cm}^3$ . Polymerization took place on the oil bath, the electron paramagnetic resonance was studied at  $10^\circ\text{C}$  to determine the free radicals.

Card 1/10

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S/190/61/003/006/013/019  
B110/B208

Study of free radical reactions.  
III. Recombination of ...

The kinetics of the recombination of the radicals  $\dot{R}$  and  $\dot{RO}_2$  was determined at different temperatures and degrees of crystallinity (74 and 46 %) (Fig. 1). The relative concentration  $I$  was referred to the initial concentration = 1:  $I_\alpha = [\dot{RO}_2]/[\dot{RO}_2]_0$ ,  $I_\beta = [R]/[R]_0$ . The reciprocal concentration as a function of time (Fig. 1) approaches linearity asymptotically corresponding to the bimolecular recombination reaction. In polymers with crystalline and amorphous phases (polyethylene, polypropylene, Teflon) recombination proceeds according to the bimolecular law with different rates in the amorphous and crystalline phase. Assuming that  $[\dot{R}]_{\text{cryst}} = c_1$ ;  $[\dot{R}]_{\text{am}} = c_2$  in the case of Teflon, the mean concentration  $c_{\text{mean}} = c_1\alpha + c_2(1 - \alpha)$ , where  $\alpha$  = degree of crystallinity.  $c_1$  and  $c_2$  depend on the time:  $\partial c_{1,2}/\partial t = -k_{1,2}c_{1,2}^2$  (2). According to  $\lim_{t \rightarrow 0} (1/I)$

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S/190/61/003/006/013/019  
B110/B208

Study of free radical reactions.  
III. Recombination of ...

$= 1 + (1 - \alpha)k_2t$  initially a rectilinear section appears in the coordinates reciprocal concentration-time (Fig. 15, curve 1), which corresponds to the square recombination in the amorphous zone, as well as a section corresponding to the square recombination in the crystalline zone in the case of higher  $t$ -values. According to (2) the straight line corresponding to the recombination in the crystalline phase cuts off the section  $1/\alpha$  on the  $y$ -axis. The degree of crystallinity may thus be determined from the recombination kinetics. Table 1 gives the degrees of crystallinity calculated from the recombination kinetics  $\dot{R}O_2$  and  $\dot{R}$ , and the  $\alpha$ -values calculated from the specific weight (according to  $d = 2.00 + 0.31\alpha [g/cm^3]$ ). Their agreement confirms the model suggested and the equality of the initial combination in both phases. The different stability of the radicals in amorphous and crystalline phase is confirmed by their decrease in concentration by 25-50 % during

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III. Recombination of ...

primary heating of the irradiated samples to 150-200°C, and constancy of the concentration of repeated heating. According to (2), the rate constants of the recombination reactions at different temperatures and degrees of crystallinity can be determined from the linear anamorphisms of the kinetic curves of the type of Figs. 1, a and 5. The recombination of fluoroalkyl radicals takes place in a measurable rate only at temperatures which are by 50-70°C higher than in the case of peroxide radicals. The following is written: peroxide radicals:

$$k_{kr}^{(46)} \approx 10^{-8} \cdot \exp \left\{ - \frac{28000 \pm 3000}{RT} \right\}; \quad (A)$$

$$k_{at}^{(46)} \approx 10^{-10} \cdot \exp \left\{ - \frac{12000 \pm 2000}{RT} \right\};$$

fluoroalkyl radicals:  $k_{kr}^{(46)} \approx 10^{-5} \cdot \exp \left\{ - (40,000 \pm 4,000)/RT \right\}$   
 $k_{at}^{(46)} \approx 10^{-7} \cdot \exp \left\{ - (30,000 \pm 3,000)/RT \right\}.$

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B110/B208

Study of free radical reactions.  
III. Recombination of ...

The activation energy of peroxide radical recombination is  $26 \pm 3$  kcal/mole in the crystalline phase,  $11 \pm 3$  kcal/mole in the amorphous phase. Values of 20 - 40 kcal/mole are obtained for primary alkyl radicals in various hydrocarbon polymers. The recombination of long-life radicals of solid polymers is not determined by their structure but by the properties of the medium: movement of the segments of polymer chains. In the amorphous phase with high chain mobility the recombination rate is determined by rotation of small chain parts. In the crystalline phase with firmly bound chains it is determined by the rotation of long chain parts. In the recombination rate of fluorocalkyl radicals the high values of the pre-exponential factors are remarkable, which have also been observed in other polymers (Table 2). The activation energy and the pre-exponential factor highly differ for various Teflon samples, which was also observable in many reactions of the solid phase and of the electric conductivity. The linear dependence  $\log k^0(E)$  existing in this case is called compensation dependence (Fig. 3). The potential barrier of the segment rotation of the polymer chain probably decreases with a rise in temperature, which

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B110/B208

Study of free radical reactions.  
III. Recombination of ...

explains the compensation dependence and the high pre-exponential factors, whose real values are  $10^{-8}$  and  $10^{-10}$  cm<sup>3</sup>/sec. The high values obtained experimentally are thus a result of the change in activation energy with temperature rise. The authors thank G. G. Titova for her assistance in some experiments. There are 3 figures, 2 tables, and 13 references: 8 Soviet-bloc and 4 non-Soviet-bloc. The most important references to English-language publications read as follows: Ref. 4: S. Ohnishi, I. Nitta, J. Polymer Sci., 38, 451, 1959. Ref. 5: Z. Kuri, H. Ueda, S. Shida, J. Chem. Phys., 32, 371, 1960. Ref. 7: J. A. Sauer, A. E. Woodward, Rev. Mod. Phys., 32, 88, 1960.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR).  
Institut khimicheskoy kinetiki i goreniya CO AN SSSR (Institute of Chemical Kinetics and Combustion of the Siberian Division AS USSR)

Card 6/10



BUBNOV, N.N.; VOYEVODSKIY, V.V.; FOK, N.V.; SHEIMOV, B.N.

Study of electron phototransfer reactions in the solid phase  
by the electron paramagnetic resonance method. Opt. i spektr.  
11 no.1:78-83 JI '61. (MIRA 14:10)  
(Paramagnetic resonance and relaxation)  
(Photomuclear reactions)

S/076/61/035/001/011/022  
B004/B060

AUTHORS: Poltorak, V. A. and Voyevodskiy, V. V.

TITLE: Kinetics of propane cracking in the presence of oxygen additions. I. Dependence on the treatment of the vessel surface with HF

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 1, 1961, 176-180

TEXT: Experiments conducted by Z. K. Mayzus, V. G. Markovich, and M. B. Neyman (Ref. 2) have shown that small oxygen additions (about 0.15%) greatly accelerate the butane decomposition. The authors of the present paper have earlier advanced (Ref. 3) a hypothesis concerning the heterogeneous character of the formation and destruction of radicals of the cracking reaction of hydrocarbons. According to this hypothesis, the effect of oxygen would also be based upon a heterogeneous process. A study has been made here of the effect of oxygen additions upon the propane cracking with and without NO additions. The vessel walls were either left untreated or were treated with boiling HF. The experiments were conducted in a quartz-vacuum apparatus. The initial propane pressure was 30-60 mm Hg, and the

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B004/B060

# Kinetics of propane cracking in ...

temperature was 600°C. The effect of NO was found to be independent of the succession provided for its addition (prior or after O<sub>2</sub>). Experimental data are given in Figs. 1,2. A treatment of the vessel walls with HF increases the effect of the oxygen addition upon the cracking. When the HF-treated vessel was checked with nontreated quartz, the reaction rate dropped from curve 3 to curve 1 of Fig. 1. The initial rate  $w$  of cracking follows the law  $w \sim (C_3H_8)^2$ . For initial C<sub>3</sub>H<sub>8</sub> pressure of 30, 40, 50, and 60 mm Hg, a ratio of reaction rates 0.1 : 1 : 1.5 : 2.3 was found. It follows from Fig. 2 that slight NO admixtures have an accelerating effect. The results are discussed on the basis of the hypothesis of the heterogeneous formation of radicals. Equations are derived for the reaction rate in the presence of O<sub>2</sub>:  $w = B(O_2) / [1 + C(O_2)]$  and for the presence of NO:  $w_{rO}^0 = B_1(NO) / [1 + C_1(NO)]^2$ . The curves determined experimentally were obtained by a suitable choice of constants B, C, B<sub>1</sub>, and C<sub>1</sub>. There are 2 figures and 4 references: 3 Soviet-bloc and 1 non-Soviet-bloc.

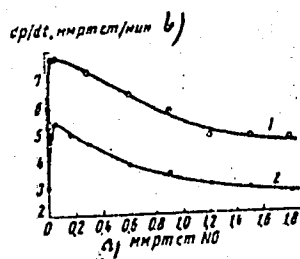
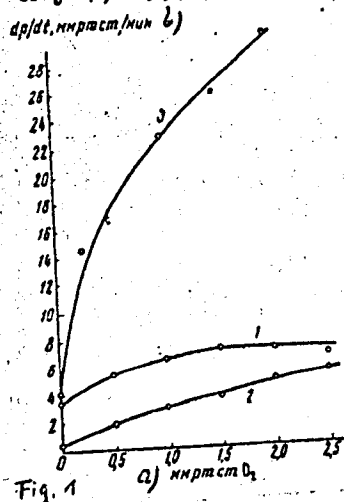
Card 2/4

Kinetics of propane cracking in ...

S/076/61/035/001/011/022  
B004/B060

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova  
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: May 7, 1959



Card 3/4

Kinetics of propane cracking in ...

S/076/61/035/001/011/022  
B004/B060

Legend to Fig. 1. 1:  $C_3H_8$ , vessel untreated; 2:  $C_3H_8 + 20\% NO$ , vessel treated with HF; 3:  $C_3H_8$ , vessel treated with HF; a) mm Hg  $O_2$ ; b) mm Hg/min.

Legend to Fig. 2. 1: 50 mm Hg  $C_3H_8$ ; 2: 40 mm Hg  $C_3H_8$ ; a) mm Hg NO; b) mm Hg/min.

✓

Card 4/4

15 8114 2209  
24 3600 (1035, 1138, 1482)

23854  
S/020/61/157/006/013/020  
B103/B217

AUTHORS:

Nesmeyanov, A. N., Academician, Korshak, V. V., Corresponding Member AS USSR, Voyevodskiy, V. V., Corresponding Member AS USSR, Kochetkova, N. S., Sosin, S. L., Materikova, R. B., Bolotnikova, T. N., Chibrikov, V. M., and Bazhin, N. M.

TITLE:

Synthesis and some optical-magnetic properties of polyferrocenes

PERIODICAL:

Doklady Akademii nauk SSSR, v. 137, no. 6, 1961, 1370-1373

TEXT: The authors studied the magnetic properties of ferrocene derivatives:

1) of the polyferrocenylenes (Table 1, nos. 1-6), 2) the polydiisopropylferrocene (Table 1, nos. 7-8), 3) the polymethano- and 4) the polyethanopolyferrocenes (Table 1, nos. 9-13). They were synthesized by: A) Polyrecombination. To 1) and 2). 1 mole ferrocene (or of its diisopropyl homolog) was treated with 1 mole tertiary butyl peroxide in nitrogen atmosphere at 200°C. 1) and 2) are assumed to be formed as follows: the Butoxyl and methyl radicals formed during peroxide decomposition separate the hydrogen from ferrocene (or the  $\alpha$ -hydrogen). The radicals thus formed

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S/020/617137/006/013/020  
B103/B217

Synthesis and some ...

recombine and form linear 1) or 2), easily soluble in benzene. An insoluble polymer (Table 1, nos. 5-6) with a two- or tridimensional network structure is formed simultaneously. The conversion of ferrocene to high-molecular products amounted to 25%. Nos. 1-3 have a softening temperature of 290-300°C and are a dark-red powder, whereas nos. 5-6 had their softening temperature at about 400°C and were light-yellow. B) Polyalkylation of ferrocene by methylene chloride and 1,2-dichloroethane in the presence of anhydrous aluminum chloride. Aluminum chloride solution in 50 ml of dihalogen alkane was added gradually to 40 g ferrocene dissolved in 250 ml dry dihalogen alkane. The mixture was stirred for 6 hr at the boiling temperature of the solvent. The next day, 10 g aluminum chloride in 25 ml dihalogen alkane were added and treated for 6 hr as above. The mixture was decomposed by ice and HCl and treated with sodium sulfite. The obtained 3) and 4) were well soluble in benzene, differed, however, by their solubility in ether. Table 1 shows the molecular weights, the always equal g-factor and the magnetic characteristics of all substances produced. The decomposition temperature of 9-13 was 115-120°C. All substances are amorphous powders, nos. 9 and 10 light-yellow, no. 11 grey-brown. Nos. 10 and 11 are of a chemical composition similar to that of no. 9 (pentaethanodiferrocene).

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B103/B217

Synthesis and some ...

They consist possibly of 2 and 4 molecules similar to the latter, connected by ethane bridges. 4-5 methylenes in the molecule of nos. 12 and 13 belong to 2 ferrocene radicals. They do not contain halogen. The infrared spectra of nos. 9-13 have frequencies within the range  $1000-1100\text{ cm}^{-1}$ . To 1). Derivatives 1) having a  $\pi$ -conjugation between the ferrocene links give a signal the electron paramagnetic resonance (e-p-r), similarly to the poly-aromatic hydrocarbons. This cannot be explained by the presence of a corresponding quantity of the oxidized form of the ferricinium cation. Table 1 shows that also polymers in which the ferrocene links are separated by the  $-\text{CH}_2-\text{CH}_2-$  group give an e. p. r. signal. It is known that the

delocalization of the unpaired electrons between the two phenyl rings is not prevented by this group. In the substances described here, which give an e. p. r. signal, this signal is the smaller, the smaller the number of ferrocene links is. This signal vanishes in 2). Polymers with a low molecular weight give no e. p. r. signal in the solution (benzene), but in solid state. This is explained by the fact that the intramolecular interactions cause in solid state a conjugation of the adjacent polymer molecules. This causes for its part an e. p. r. signal. All polymers

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B103/B217

Synthesis and some ...

giving this signal show a single symmetrical line of the e. p. r. of the Lorenz type. The 1) obtained from the reaction A yields a wide e. p. r. line of 120-160 oersteds, its width being dependent on the polymer structure. This line becomes broader on reducing the measuring temperature. Its width is changed most considerably in low-molecular polymers. The authors believe the nature of the measured signals to be unclarified, they cannot maintain that the number N of the unpaired electrons per 1 member, determined by a comparison with the standard, corresponds to their actual number. N may, however, be a certain characteristic of the magnetic properties of the system. (nos. 2-4). N reaches an anomalous size in the insoluble polymer no. 5. This is assumed to be connected with a collective effect of the ferromagnetic type. The ultraviolet (UV-) spectra of 1) dissolved in n-octane, which give an e. p. r. signal in solid state, differ from the ultraviolet spectra of such that give no signal in solid state. In the first case the UV-spectrum agrees completely with that of ferrocene dissolved in  $\text{CCl}_4$ . It was proved for these spectra (Ref. 7) that the charge transfer takes place here under formation of an ion pair  $\text{Fer}^+\text{CCl}_4^-$ . On the contrary, the UV-spectrum of such 1) that give no e. p. r. signal is similar

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B103/B217

Synthesis and some ...

to that of ferrocene in a neutral solvent (n-octane), i. e. under conditions under which the charge is not transferred. Finally, the authors point out that their results concerning the UV-spectra apparently confirm the "pseudoferrromagnetism" of the polynucleotides and of the polyaromatic hydrocarbons (Refs. 5 and 8). There are 1 figure, 1 table, and 8 references: 7 Soviet-bloc and 1 non-Soviet-bloc. The only reference to English-language publication reads as follows: J. C. D. Brand, Ref. 7: Trans. Farad. Soc., 53, 894, 1957.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR  
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: December 20, 1960

Legend to Table 1. I) Current number, 1-4) linear polyferrocenylene, 5-6) insoluble polyferrocenylene, 7) polydiisopropylferrocene, linear, 8) like 7, insoluble, 9-11) condensation products of ferrocene with Di-1,2-chloroethane, 12-13) with methylene chloride, 14) ferricinium cation. II) Substance, III) molecular weight, IV) g-factor, V-VI) line width, oersted

Card 5/6

TOLKACHEV, V.A.; MOLIN, Yu.N.; CHKHEIDZE, I.I.; BUBEN, N.Ya.;  
VOYEVODSKIY, V.V.

Electron paramagnetic resonance spectrum of frozen irradiated  
benzene. Dokl. AN SSSR 141 no.4:911-912 D '61. (MIRA 14:11)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy  
kinetiki i goreniya Sibirskogo otdeleniya AN SSSR. 2. Chlen-kor-  
respondent AN SSSR (for Voyevodskiy)..  
(Benzene—Spectra)

16  
WAVEVODSKIY, V. V.

807/6177  
PHASE I BOOK EXPLOITATION

Akademiya nauk SSSR. Institut neftekhimicheskogo sinteza

Radioliz uglevodorodov; nekotoryye fiziko-khimicheskiye problemy  
(Radiolysis of Hydrocarbons; Some Physicochemical Problems)  
Moscow, Izd-vo AN SSSR, 1962. 207 p. Errata slip inserted.  
5000 copies printed.

Resp. Eds.: A. V. Topchiyev, Academician, and L. S. Polak,  
Doctor of Physics and Mathematics; Ed.: L. T. Bugayenko;  
Tech Ed.: Ch. A. Zentsel'skaya.

PURPOSE: This book is intended for physical and industrial chemists  
interested in the properties and behavior of irradiated hydro-  
carbons.

COVERAGE: The book gives a systematic presentation of the results  
of research on the radiolysis of hydrocarbons carried out from  
1957 through 1961 at the Laboratory of Radiation Chemistry,  
Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petro-

Card 1/4

Radiolysis of Hydrocarbons (Cont.)

SOV/6177

chemical Synthesis, Academy of Sciences USSR). Although the results were obtained for individual compounds, they may be generalized and applied to other members of the same homologous series. The following persons participated in making the experiments and in writing the text: V. G. Beryezkin, V. E. Glushnev, Yu. A. Kolbanovskiy, I. M. Kustanovich, V. D. Popov, A. Ya. Temkin, V. D. Timofeyev, N. Ya. Chernyak, V. A. Shakhray, E. B. Shlikhter, A. S. Shcherbakova, E. M. Negodov, A. Z. Peryshkina, M. M. Kytova, T. A. Tgina, Yu. B. Emin, A. M. Bredskiy, V. V. Voyevodskiy, P. Ya. Glazunov, B. A. Smirnova, and Yu. L. Khaik. References, mainly Soviet and English, follow individual chapters.

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Foreword	3
Ch. I. Physicochemical Characteristics of Hydrocarbon Radiolysis	5
Card 2/4	

LEBEDEV, Ya.S.; CHERNIKOVA, D.M.; TIKHOMIROVA, N.N.; VOYEVOVSKIY,  
V.V., otv. red.; BUTOMO, N.N., red. izd-va; SIMKINA, G.S.,  
tekhn. red.; POLENOVO, T.P., tekhn. red.

[Atlas of electron paramagnetic resonance spectra; theoretical-  
ly computed multicomponent symmetric spectra] Atlas spektrov  
elektronnogo paramagnitnogo rezonansa; teoreticheski rasschi-  
tannye mnogokomponentnye simmetricheskie spektry. Moskva, Izd-  
vo Akad. nauk SSSR, 1962. 228 p. (MIRA 15:12)

1. Akademiya nauk SSSR. Institut khimicheskoy fiziki. 2. Labo-  
ratoriya khimicheskoy radiospektroskopii Instituta khimicheskoy  
fiziki Akademii nauk SSSR (for Lebedev, Chernikova, Tikhomirova).  
(Paramagnetic resonance and relaxation—Spectra)

PHASE I BOOK EXPLOITATION

SOT/6495

Blyumenfel'd, Lev Aleksandrovich, Vladislav Vladislavovich Voyevodskiy, and  
Anatoliy Grigor'yevich Semenov

Primeneniye elektronogo paramagnitnogo rezonansa v khimii (Use of Electron  
Paramagnetic Resonance in Chemistry) Novosibirsk, Izd-vo Sibirskogo  
Otdeleniya AN SSSR 1962. 239 p. 10,000 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Sibirskoye otdeleniye. Institut  
khimicheskoy kinetiki i goreniya So. AN SSSR. Institut khimicheskoy  
fiziki AN SSSR.

Ed.: T. M. Nazaryants; Tech. Ed.: O. A. Lokshina.

PURPOSE: This book is intended for scientists using Electron Paramagnetic  
Resonance technique in chemistry as a research tool.

COVERAGE: This advanced textbook covers the fundamentals of EPR technique in  
chemical research. It is based on Soviet and non-Soviet literature and on

Card 1/6  
2

## Use of Electron Paramagnetic (Cont.)

804/6495

the work of the authors. The first part of the book discusses questions of experimental technique, theory of the method, and analysis of experimental data and the principles of building EPR spectrometers, particularly the serial-type EPR-2 spectrometer used in the USSR. The modern theory of EPR method and the theoretical physics involved, i.e. group theory, quantum mechanics, etc., are presented. The second part of the book deals with the application of EPR technique in solving a series of problems in modern chemical reactions and the study of intermediate compounds and elemental processes. This book is not a complete review of the field, but is restricted to the illustration of concrete examples based on the authors' contributions in this field and to conclusions generalized from these works. The book reportedly does not overlap the existing monographs on EPR. There are 309 references, 121 Soviet and 188 non-Soviet.

## TABLE OF CONTENTS [Abridged]:

Preface

3

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2



L322h

S/844/62/000/000/014/129  
D290/D307

5.4600

AUTHOR: Voyevodskiy, V. V.

TITLE: On the mechanism of the radiolysis of water

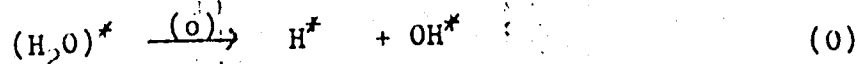
SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962,  
102 - 108

TEXT: The author considers the fact that very small quantities ( $\sim 10^{-5}$  M) of various impurities appreciably alter the yields of radiolysis products from water, and that increases in impurity concentrations above a certain critical value cease to affect the yields; he suggests that this effect is caused by the influence of the impurity on the transfer of the initial excitation. It is regarded that no theory attempting to explain these effects is completely satisfactory. It is suggested that excited water molecules always split into two excited radicals: X

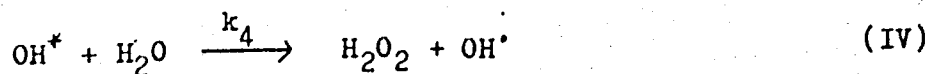
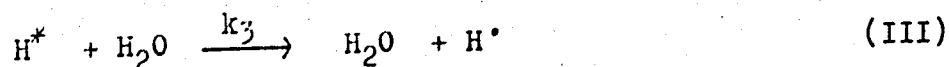
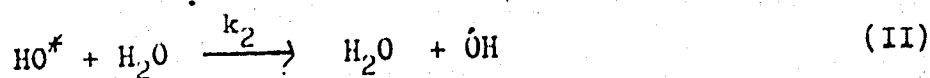
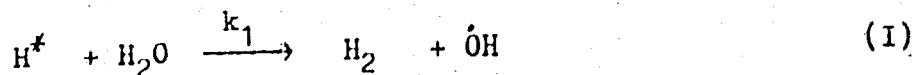
Card 1/3

S/844/62/000/000/014/129  
D290/D307

On the mechanism of ...



which react extremely rapidly, according to the following equations:



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D290/D307

On the mechanism of ...

The cycle of processes (0) - (IV) enables the yields of the four main products of the radiolysis of water ( $H_2$ ,  $H_2O_2$ , H, and OH) to be expressed in terms of the yield of process (0) and the ratios  $k_1/k_3$  and  $k_2/k_4$ . Predictions of this theory are shown to be consistent with many experimental results, and the theory itself explains the radical nature of the radiolysis of water, the great effect of small impurity concentrations, the molecular products, and the hitherto unexplained differences in the yields of the various products. ✓

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya SO AN SSSR  
(Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS USSR)

Card 3/3

S/844/62/000/000/055/129  
D204/D307

AUTHORS: Molin, Yu. N., Chhkeidze, I. I., Buben, N. Ya. and Voyevodskiy, V. V.

TITLE: A study of the transfer of energy to aromatic groups during the radiolysis of some organic compounds, by the EPR method


SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 326-330

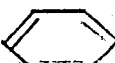
TEXT: The present work is a continuation of an earlier study in which the energy transfers in compounds of type A - D (where A is an aromatic and D an irradiation-unstable substituent) were investigated, D and A behaving respectively as donors and acceptors of energy, to allow a quantitative assessment of such energy transfers. The EPR-2 (EPR-2) apparatus was used, under a beam of 1.6 Mev electrons, the rate of irradiation being 0.03 - 0.3 Mrads/sec. The production of radicals (at 90 - 160°K) increased linearly with increasing doses of irradiation, up to a concentration of  $\sim 10^{20}$  per g. Card 1/3

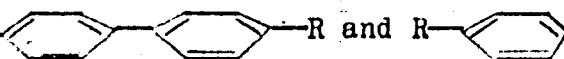

S/844/62/000/000/055/129  
D204/D307

A study of the transfer ...

The radiation yields of radicals, G, were similar in saturated hydrocarbons, as well as in those containing multiple bonds, and were of the order of a few per 100 ev of absorbed energy; they were lower (by a factor of  $10^1 - 10^2$ ) in unsubstituted aromatics than in saturated hydrocarbons and, in aromatic compounds, decreased up to a point with increasing degree of conjugation. In (A-D)-type com-

pounds (I)  R, where R = Me, Et, cyclohexyl,  $G_{AD}$  was 0.1 - 1, showing that at  $D \rightarrow A$  transfer of energy took place with a probability ( $\alpha$ ) of 65 - 95%. Energy transfers in (I) and in compounds

(II)   $(CH_2)_n SiR_3$  (where  $n = 0, 1, 2, 3$  for R = Me and 0.3 for R = Et) led in most cases to the predominance, in the EPR spectra, of lines corresponding to a primary C-H fission in the benzene

ring. In compounds (III)  R and R- R',

the EPR spectra were more complex and, with long-chain substituents, lines corresponding to bond fission in the latter began to predominate.  
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A study of the transfer ...

S/844/62/000/000/055/129  
D204/D307

minate. The results are discussed, showing that  $D \rightarrow A$  energy transfers occur in all 3 classes of compounds, with high values of  $\alpha$ . The assistance of G. K. Voronova and of Ye. D. Kaplan, Ye. A. Chernyshev and V. F. Mironova, members of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry, AS USSR), is acknowledged. There are 2 figures and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR); Institut khimicheskoy kinetiki i goreniya SO AN SSSR (Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS USSR)

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S/844/62/000/000/089/129  
D204/D307

AUTHORS: Tscvetkov, Yu. D., Lebedev, Ya. S. and Voyevodskiy, V. V.  
TITLE: A study of radical recombinations in irradiated teflon  
SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 521-525

TEXT: The kinetics were studied of the recombinations of fluoroalkyl ( $\dot{R}$ ) and peroxide ( $RO_2$ ) radicals, formed when polytetrafluoroethylene (teflon) is irradiated with  $\gamma$  rays, in vacuum or under  $O_2$ , as this field is as yet incompletely explored. EPR spectroscopy was employed to follow the reactions in specimens in which the degree of crystallinity,  $\alpha$ , was 46 or 74%. The reactions were always of the 2nd order, but the velocity constants ( $k^0$ ) depended on  $\alpha$ . Thus for  $\dot{R}$  radicals, with  $\alpha = 74\%$ ,  $k^0 = 10^6$ , and with  $\alpha = 46\%$ ,  $k^0 = 10^{-3}$  cm<sup>3</sup>/sec. A linear relation was observed between  $\log k^0$  and  $E_{eff}$ .

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D204/D307

A study of radical ...

the effective activation energies, which were between  $30 \pm 3$  and  $65 \pm 5$  and between  $10 \pm 2$  and  $26 \pm 3$  kcal/mole for  $\dot{R}$  and  $\dot{RO}_2$  radicals respectively. The pre-exponential constants were anomalously high. To explain the observed phenomena, it is suggested that the activation energy, which apparently depends on the potential barrier for the rotation of polymeric chain segments, decreases with increasing temperature ( $180 - 270^\circ\text{C}$  for  $\dot{R}$ , and  $110 - 200^\circ\text{C}$  for  $\dot{RO}_2$ , i.e. for teflon irradiated under oxygen). The theoretical results may be of use in the study of solid state reactions exhibiting a compensating effect and abnormally high pre-exponential multipliers. There are 2 figures and 2 tables.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR; Institut khimicheskoy kinetiki i goreniya SO AN SSSR (Institute of Chemical Physics, AS USSR; Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS USSR)

Card 2/2



S/844/62/000/000/113/129  
D207/D307

AUTHORS: Kazanskiy, V. B., Pariskiy, G. B. and Voyevodskiy, V. V.

TITLE: An EPR study of the properties of hydrogen atoms and of defects formed on the irradiation of silica gel

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 656-659

TEXT: Silica gel was investigated because of its special adsorption and catalytic properties. The gel had a specific surface area of 200 m<sup>2</sup>/g and contained less than 0.1% Fe and Al impurities. It was irradiated with Co<sup>60</sup>  $\gamma$  rays, in vacuum, at -196°C and at room temperature, with doses of 5 - 10 megarads. After irradiation at -196°C the EPR spectrum (recorded at the same temperature) indicated the presence of radiation defects and free hydrogen atoms, the latter being formed by radiolysis of the surface OH groups; the H-atom concentration increased with the temperature (200 - 500°C) to which the gel was heated before irradiation. On vacuum

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D207/D307

An EPR study ...

heating to  $-150$  and  $-120^{\circ}\text{C}$  after irradiation, hydrogen atoms recombined slowly into molecules, the recombination being hindered by the location of atoms in deep pores or microcracks in the gel surface. Heating to  $-150$  and  $-120^{\circ}\text{C}$  in ethylene and oxygen removed the free hydrogen atoms by chemical reactions as well as by recombination. Vacuum heating to  $200 - 300^{\circ}\text{C}$  for 8 hours, followed by vacuum irradiation at room temperature, gave a quintuplet EPR spectrum with a g-factor identical with that of phenyl picryl hydrazyl. The hyperfine structure of the spectrum was due to the interaction between an unpaired electron of a radical and protons of four OH surface groups. Vacuum heating of silica gel to  $500^{\circ}\text{C}$  followed by room-temperature irradiation in vacuum, generated volume defects similar to F-centers and consisting of electrons captured by oxygen vacancies. Acknowledgments are made to Corresponding Member of the Academy of Sciences of the USSR, G. K. Boreskov, and to Yu. A. Mishchenko of the Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ya. Karpov). There are 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR)  
Card 2/2

PECHERSKAYA, Yu.I.; KAZANSKIY, V.B.; VOYEVODSKIY, V.V.

Electron paramagnetic resonance studies of the thermal activation  
of chromium gel. Kin.i kat. 3 no.1:111-113 '62. (MIRA 15:3)

1. Institut khimicheskoy fiziki AN SSSR.  
(Chromium) (Catalysis)

VOYEVODSKIY, V.V.

Some problems of present-day chemical kinetics. Kin. i Kat.  
3 no.5:627-632 8-0 '62. (MIRA 16:1)

1. Institut khimicheskoy kinetiki i goreniya Sibirskogo  
otdeleniya AN SSSR.  
(Chemical reaction, Rate of) (Catalysis)

42168

S/195/62/003/005/002/007  
EO75/E436

11.9200 (also 4223)  
11.0132

AUTHORS: Molin, Yu.N., Chkheidze, I.I., Kaplan, Ye.P.,  
Buben, N.Ya., Voevodskiy, V.V.

TITLE: Formation of radicals during radiolysis of solid  
organic materials. Part I. Comparison of radical  
yields in various organic compounds

PERIODICAL: Kinetika i kataliz, v.3, no.5, 1962, 674-679

TEXT: The work was carried out to establish a connection  
between molecular structure and probability of its dissociation  
into radicals under the action of high energy radiation.  
A series of naphthenic and hydroaromatic hydrocarbons with  
non-conjugated unsaturated bonds were investigated as well as  
some aromatic compounds (di- and triphenyls and phenyl ethers).  
The purity of the compounds was 95 to 99%. The solids were  
irradiated with fast electrons, the dosage varying between 0.02  
and 1 Mrads/sec. Maximum dosage reached 30 Mrads. The yields  
of free radicals were determined by electron paramagnetic  
resonance at -170 to -110°C using the initial linear part of the  
curves relating the numbers of radicals formed to time of  
Card 1/3

Formation of radicals ...

S/195/62/003/005/002/007  
E075/E436

irradiation. It was found that for naphthenic and hydroaromatic hydrocarbons the yields amounted to several radicals per 100 eV of absorbed energy. A large yield was also obtained for n-hexadecene-1. Thus the unsaturated bonds in these compounds do not inhibit the radical formation. This conclusion does not agree with that obtained by A. Charlesby and M.G. Ormerod (V. Intern. Symp. on Free Radicals, Uppsala, 1961, paper 11). For the aromatic compounds the yields are smaller by 1 to 2 orders of magnitude. The yields decrease with the increasing number of conjugated double bonds in aromatic molecules and with the increasing degree of substitution of benzene rings with groups containing unshared electron pairs or multiple bonds conjugated with the aromatic system of the molecule. It is concluded that the yield of radicals  $G_R$  decreases with the decreasing first excitation energy level  $E_1$ . Especially marked changes in the yield are observed when  $E_1 \approx DCH$ , where  $DCH$  is the energy of rupture of a C-H bond. There are 1 figure and 2 tables.

ASSOCIATIONS: Institut khimicheskoy fiziki AN SSSR  
(Institute of Chemical Physics AS USSR)

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Formation of radicals ...

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E075/E436

Institut khimicheskoy kinetiki i goreniya  
SO AN SSSR (Institute of Chemical Kinetics and  
Combustion SO AS USSR)  
Institut organicheskoy khimii AN SSSR  
(Institute of Organic Chemistry AS USSR)

SUBMITTED: May 9, 1962

Card 3/3

S/190/62/004/012/002/015  
B101/B186

AUTHORS: . Skuratov, S. M., Yenikolopyan, N. S., Bonetskaya, A. K.,  
Voyevodskiy, V. V.

TITLE: Mechanism of lactam polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962,  
1770-1778

TEXT: In continuation of papers of 1952-54 (last publication Dokl. AN SSSR, 95, 1017, 1954), the polymerization of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam was studied in the presence of water, water and acid, and water and alkali at 231.5°C. A slightly modified reaction scheme is proposed on the basis of experimental results concerning induction period, maximum reaction rate, time before maximum reaction rate is reached, degree of conversion, heat

effect of the reaction: (1)  $B + H_2O \xrightleftharpoons[k_1]{k_1} AH$ ; (2)  $AH + AH \xrightarrow{k_2} P + H_2O$ ; ✓

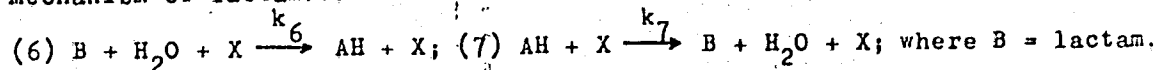
(3)  $AH + P \xrightarrow{k_3} P + H_2O$ ; (4)  $AH + B + X \xrightarrow{k_4} P + X$ ; (5)  $B + P \xrightarrow{k_5} P$ ;

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B101/B186

Mechanism of lactam...



AH = amino acid, P = polyamide, X = catalyst. The probable course of these reactions under different conditions is discussed, and the following equations are derived for the rate of polymerization, w: (A) for polymeriza-

tion of  $\epsilon$ -caprolactam in the presence of  $H_2O$ :  $w = \alpha' [H_2O] [B] ([B_0]^2 - [B]^2)$ ,

where  $\alpha' = k_4 k_6 / 2k_7$ ; (B) for polymerization of  $\gamma$ -enantholactam in the presence of water:  $w = \alpha' [H_2O] [B] \sqrt{[B_0]^2 - [B]^2}$ ; where  $\alpha' = k_5^{0.5} k_2^{0.5} k_6 / k_3$ ;

(C) for polymerization of  $\epsilon$ -caprolactam in the presence of  $H_2O$  and  $H_3PO_4$ :

$w = \beta' \sqrt[4]{[AcH] [B]} \sqrt{[B_0]^2 - [B]^2}$ , where  $\beta' = (k_4 k_5 k_6 [H_2O] / k_7)^{0.5}$ , and

AcH = acid; (D) for polymerization of  $\gamma$ -enantholactam in the presence of  $H_2O$  and  $H_2PO_4$ :  $w = \alpha' \sqrt[4]{[AcH] [B]} \sqrt{[B_0]^2 - [B]^2}$ , where

$\alpha' = k_2^{0.25} k_5^{0.75} k_6^{0.5} [H_2O]^{0.5} / k_3^{0.5}$ ; (e) in the polymerization of  $\epsilon$ -caprolactam and  $\gamma$ -enantholactam in the presence of  $H_2O$  and NaOH, the presence of

Card 2/3

Mechanism of lactam...

S/190/62/004/012/002/015  
B101/B186

NaOH only reduces the induction period without affecting the polymerization kinetics proper. All the experimental results are satisfactorily explained by these equations. There are 3 tables.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova  
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: June 24, 1962

Card 3/3

VOYEVODSKIY, V.V.; BLYUMENFEL'D, L.A., doktor khimicheskikh nauk

Weak interactions in organic chemistry. Zhur. VKHO 7 no.4:  
457-461 '62. (MIRA 15:8)

1. Chlen-korrespondent AN SSSR.  
(Chemistry, Organic)

S/051/62/012/001/005/020  
E075/E436

AUTHORS: Solodovnikov, S.P., Voyevodskiy, V.V.

TITLE: Application of the analysis of line form in electronic paramagnetic resonance for the investigation of density distribution of unpaired electron in the anions of some polymers

PERIODICAL: Optika i spektroskopiya, v.12, no.1, 1962, 32-36

TEXT: The authors investigated densities of delocalized unpaired electrons in a number of polyphenyl molecules. The polymer molecules were converted into anions by interacting of aromatic hydrocarbons with metallic calcium dissolved in 1,2-dimethoxyethane. Spectra of e.p.r. were taken at room temperature, the concentration of the paramagnetic particles being about  $10^{-4}$  mole. For the different polymeric anions examined, lines with a diffuse hyperfine structure were obtained alongside with the spectra containing resolved hyperfine structure. A direct method of the evaluation of degree of delocalization of unpaired electron was used for the interpretation of the experimental results. The line width observed experimentally is expressed by

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